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SUPPORTING INFORMATION

Interpretation of transition voltage spectroscopy

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a. Analytical expression for V_m using Stratton. We start with eq. 1 in the main text, which expresses the current through a rectangular barrier:

$$I \propto \sinh\left(\frac{eV\tau}{\hbar}\right)$$

To find V_m , we put the derivative in a Fowler-Nordheim plot to zero. Substituting $y = 1/V$, we find:

$$\begin{aligned} \frac{d\ln(I/V^2)}{d(1/V)} &= \frac{d}{dy}(\ln(\sinh(\frac{e\tau}{y\hbar})) + 2\ln(y)) \\ &= \frac{2}{y} - \frac{e\tau}{\hbar} \frac{1}{y^2} \coth(\frac{e\tau}{\hbar y}) = 0. \end{aligned}$$

Thus:

$$y_m = \frac{e\tau}{2\hbar} \coth\left(\frac{e\tau}{\hbar y_m}\right)$$

By re-substituting $y_m = 1/V_m$, equation 2 in the main text is obtained.

b. Full formulation of the Simmons formula. According to ref [1], a full expression for the current density, J , through a barrier between two similar metal electrodes over the entire voltage range is given by:

$$\begin{aligned} J &= c\{\tilde{A} + \tilde{B} + \tilde{C}\} \\ c &= \frac{4\pi me}{h^3} \\ \tilde{A} &= eV \int_0^{\eta-eV} \exp(-A\sqrt{\eta + \bar{\phi} - E_x}) dE_x \\ \tilde{B} &= -\bar{\phi} \int_{\eta-eV}^{\eta} \exp(-A\sqrt{\eta + \bar{\phi} - E_x}) dE_x \\ \tilde{C} &= \int_{\eta-eV}^{\eta} (\eta + \bar{\phi} - E_x) \exp(-A\sqrt{\eta + \bar{\phi} - E_x}) dE_x. \end{aligned}$$

Here, $A = (4\pi\Delta s/h)\sqrt{2m}$, where $\Delta s = s_2 - s_1$ is the width of the barrier at the Fermi energy of the metal and $\bar{\phi}$ is the average barrier height. In ref [1], parts of the integrands are neglected. The consequence of this is that for small A and/or small ϕ , the commonly used Simmons expression gives unphysical results. Below, we calculate the full integrands. \tilde{A} and \tilde{B} are of the same form:

$$- \int_{e_1}^{e_2} \exp(-A\sqrt{\eta + \bar{\phi} - E_x}) d(-E_x) > 0$$

By substituting $y^2 = \eta + \bar{\phi} - E_x$ and $d(-E_x) = d(\eta + \bar{\phi} - E_x) = dy^2 = 2ydy$, this becomes:

$$- \int_{y_1}^{y_2} \exp(-Ay) \cdot 2ydy$$

Here, $y_{1,2} = \sqrt{\eta + \bar{\phi} - e_{1,2}}$. These integrals can be solved by partial integration [1]. Boundaries for \tilde{A} are $e_1 = 0$, $e_2 = \eta - eV$, $y_1 = \sqrt{\eta + \bar{\phi}}$, $y_2 = \sqrt{\bar{\phi} + eV}$, yielding:

$$\tilde{A} = \frac{2eV}{A^2} \{ (A\sqrt{\bar{\phi} + eV} + 1) \exp(-A\sqrt{\bar{\phi} + eV}) - (A\sqrt{\eta + \bar{\phi}} + 1) \exp(-A\sqrt{\eta + \bar{\phi}}) \}.$$

Boundaries for \tilde{B} are $e_1 = \eta - eV$, $e_2 = \eta$, $y_1 = \sqrt{\bar{\phi} + eV}$, $y_2 = \sqrt{\bar{\phi}}$, yielding:

$$\tilde{B} = \bar{\phi} \frac{2}{A^2} \{ (A\sqrt{\bar{\phi}} + 1) \exp(-A\sqrt{\bar{\phi}}) - (A\sqrt{\bar{\phi} + eV} + 1) \exp(-A\sqrt{\bar{\phi} + eV}) \}.$$

Like \tilde{A} and \tilde{B} , \tilde{C} can again be solved by substituting $y^2 \equiv \eta + \bar{\phi} - E_x$ and $d(-E_x) = d(\eta + \bar{\phi} - E_x)$ and partial integration.

$$\tilde{C} = -2 \int_{y_1}^{y_2} y^3 \exp(-Ay) dy$$

Boundaries for \tilde{C} are $e_1 = \eta - eV$, $e_2 = \eta$, $y_1 = \sqrt{\bar{\phi} + eV}$, $y_2 = \sqrt{\bar{\phi}}$, so that:

$$\begin{aligned} \tilde{C} = \frac{2}{A} \{ & (\bar{\phi}^{3/2} + \frac{3}{A}\bar{\phi} + \frac{6}{A^2}\sqrt{\bar{\phi}} + \frac{6}{A^3}) \exp(-A\sqrt{\bar{\phi}}) \\ & - ((\bar{\phi} + eV)^{3/2} + \frac{3}{A}(\bar{\phi} + eV) + \frac{6}{A^2}\sqrt{\bar{\phi} + eV} + \frac{6}{A^3}) \exp(-A\sqrt{\bar{\phi} + eV}) \} \end{aligned}$$

Taking all integrals together, we can calculate J . Note that for relatively high and/or thick barriers, i.e. if $A\sqrt{\bar{\phi} \pm eV} \gg 1$, the full expression for J reduces to eq. (26) of reference [1]:

$$\begin{aligned} J = J_0 \{ & (\phi - eV/2) \exp(-A\sqrt{\phi - eV/2}) - \\ & (\phi + eV/2) \exp(-A\sqrt{\phi + eV/2}) \}. \end{aligned}$$

where, $J_0 = e/(2\pi\hbar s^2)$.

Figure 1 shows V_m versus $1/d$ for each of the three equations mentioned above; eq. 26 of ref [1], (black), eq. 1 (Stratton) in the main text (blue) and the full Simmons expression (red). For thick barriers all three collapse on a single line. The maximum deviation between the three is in the order of a few percent for thin barriers (around $d = 5\text{\AA}$). These differences are negligible compared to the spread in the experimental data as discussed in the Letter.

c. The inclusion of an image potential using Simmons. For the calculations including the image potential it is essential to use the full formulation of Simmons. Eq. 35 of reference [1] was used to calculate $\bar{\phi}$:

$$\bar{\phi} = \frac{1}{\Delta s} \int_{s_1}^{s_2} \left\{ \phi_0 - \frac{eVx}{s} - \frac{1.15\lambda s^2}{x(s-x)} \right\} dx.$$

Here, $\lambda = e^2 \ln 2 / 8\pi\epsilon_r s$, where ϵ_r is the dielectric constant. s_1 and s_2 are the positions where the barrier is equal to the Fermi energy of the metal and were found numerically. Figure 2 shows the dependence of V_m on d for different ϕ_0 (see figure 2a) and different ϵ_r (see figure 2b) using these equations.

d. V_m for alkanes using a simple coherent model of molecular transport. In Figure 3 of the Letter, we assumed $E_{HOMO} = -4$ eV [2]. We also calculated V_m versus d for $E_{HOMO} = -2.14$ [3] and -3 eV (see Figure 3a). V_m saturates at a voltage V_{sat} above $d > 9\text{\AA}$ for all three cases. V_{sat} scales linearly with E_{HOMO} , thereby justifying TVS as a spectroscopic tool (see Figure 3b).

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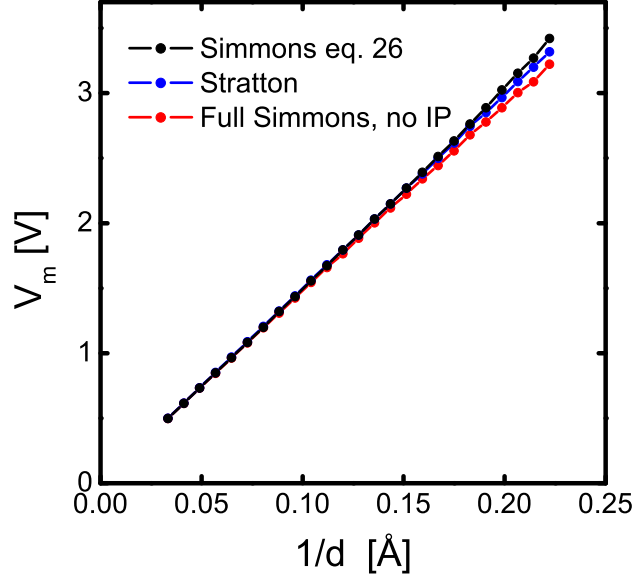


FIG. 1: V_m versus $1/d$ for a barrier with $\phi=4\text{eV}$ and $d=1\text{nm}$. Clearly, V_m is roughly proportional to $1/d$ using the three equations mentioned above; eq. 26 of ref [1] (black), eq. 1 in the main text (Stratton, blue) and the full Simmons expression (red).

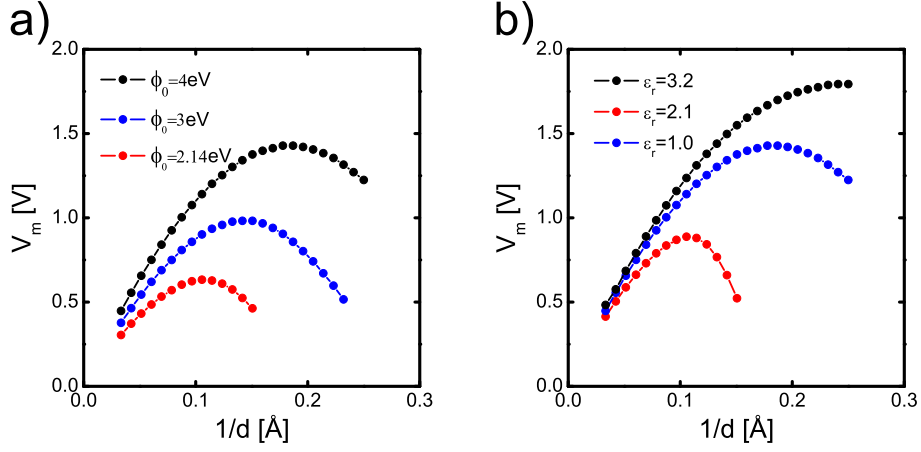


FIG. 2: V_m versus $1/d$ for **a)** different ϕ_0 (figure 2a, $\epsilon_r = 2.1$) and **b)** different ϵ_r (figure 2b, $\bar{\phi} = 4\text{eV}$) using the full Simmons expression with image potential.

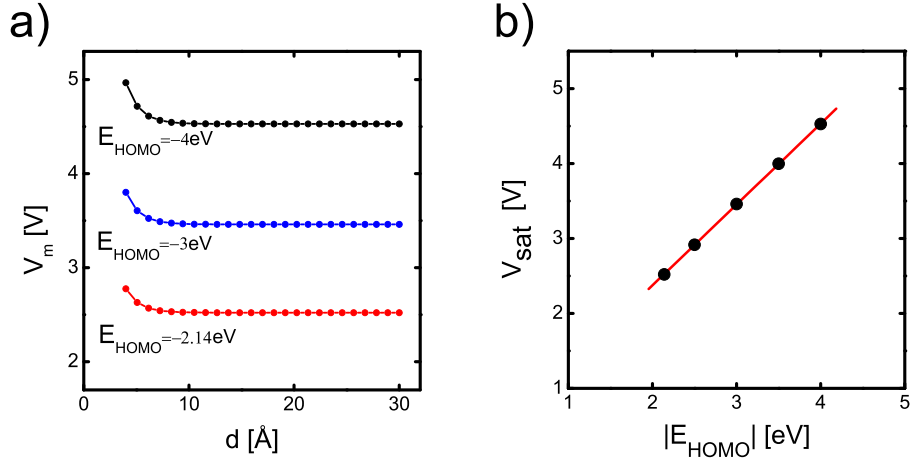


FIG. 3: **a)** V_m calculated using our coherent level model (see main text) for several positions of the HOMO. For $d > 9\text{\AA}$, V_m saturates to a value V_{sat} **b)** Plot demonstrating that V_{sat} scales linearly with the position of the molecular HOMO level.